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ATOMIC COLLISION PROCESSES RELATING TO THE IONOSPHERE

FINAL REPORT

ARPA Order Number: 125

Contract NONR-2584(00)

Period of Contract: 1 June 1958 to 31 August 1968

September 20, 1968

Office of Naval Research

Washington 25, D. C.

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Principle Scientists: A. V. Phelps and P. J. Chantry

Atomic and Molecular Sciences Research and Development  
Westinghouse Research Laboratories  
Beulah Road, Churchill Boro  
Pittsburgh, Pennsylvania 15235

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#### ABSTRACT

This final report for Contract Nonr-2584(00) entitled Atomic Collision Processes Relating to the Ionosphere consists of a summary of the more important results obtained and a set of abstracts of the technical reports published under the contract. The published results include the experimental discovery of resonances in the elastic scattering cross sections of atoms and molecules, studies of the role of resonances in the determination of vibrational and electronic excitation cross sections and of cross sections for negative ion formation, and determinations of elastic and inelastic scattering cross sections for electrons in various gases such as  $N_2$ ,  $O_2$ ,  $CO_2$ , and  $H_2O$ . Recent unpublished results concerned with electron attachment in  $O_3$  and  $N_2O$  and with the development of a new technique for the measurement of inelastic scattering cross sections are discussed.

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## ATOMIC COLLISION PROCESSES RELATING TO THE IONOSPHERE

### I. SUMMARY OF PUBLISHED PAPERS

The object of this study has been to provide basic data and understanding regarding the interaction of low and moderate energy electrons with gases. The experimental data have provided ARPA and other defense activities with some of the cross sections needed for the analysis and prediction of the performance of systems in the presence of the ionization produced in atmospheric gases by reentry wakes and nuclear explosions. This program has also provided other research groups engaged in experimental and theoretical studies of electron collision processes with new and more accurate experimental techniques, experimental evidence of the importance of resonances, and cross sections of elastic and inelastic scattering in wide range of gases used in the laboratory.

The results of the work carried out under this contract are described in the publications listed in Section III. The purposes of this summary are to provide a basis for relating the various papers to each other and to point out the significance of the work discussed in the papers. It is convenient to divide the summary into sections based on the type of electron or ion collision processes investigated. References given in this section are to the technical report numbers of the published papers of Section III of this report.

#### A. Resonances in Elastic and Inelastic Scattering Cross Sections

Experiments performed under this contract provided the first experimental evidence (16,19,24,27,30) of the presence of resonances or temporary negative ion states in the elastic scattering cross sections of gases. This work was accompanied by the first quantitative study (2,19,22) of the importance of resonances in the vibrational excitation of other gases, such as CO, N<sub>2</sub>O, H<sub>2</sub> and CO<sub>2</sub> and the electronic excitation (2,26) of gases, such as He.

Largely on the basis of this work Dr. G. J. Schulz was awarded the Davisson-Germer Prize of the American Physical Society for 1966.

#### B. Electron Attachment

Experimental studies (4,6,7,8,23,31,33,34,38) of dissociative attachment by electrons to gases, such as  $O_2$ ,  $H_2O$ ,  $O_3$ ,  $CO$ ,  $CO_2$ ,  $N_2O$  and  $H_2$  have a) provided accurate cross sections for the attachment, b) yielded data and understanding regarding the way in which the excess energy of the reaction is divided among the products, and c) led to the discovery (Section II A) of an extremely rapid temperature dependence of the attachment coefficient for near thermal electrons in  $N_2O$ . Of considerable importance to the interpretation of dissociative attachment experiments is the development (23,32) of a theory for taking into account the thermal motion of the target molecule. The application (23,32) of this theory to the analysis of dissociative attachment experiments in  $O_2$  has resolved a long-standing discrepancy between determinations of the electron affinity of atomic oxygen as determined by electron beam techniques and by photodetachment techniques.

#### C. Determination of Cross Sections from Measured Transport Coefficients

Measurements and analysis (5,9,11,12,17,20,25,28,35,37) of electron transport coefficients carried out in connection with this contract have provided a set of elastic and inelastic cross sections for low and moderate energy electrons in gases, such as  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $CO$ ,  $H_2$  and  $He$ . These cross sections can be used to predict quantities such as electron collision frequencies, electron cooling rates, and vibrational excitation rates under various conditions of temperature and density. As an example, predictions of the propagation constants for electromagnetic waves in air (3) using these cross sections differ significantly from the results based on previous less accurate cross section data.

#### D. Ion-Molecule Reactions

Experimental studies (15,36) of ion-molecule reactions in the source region of a high pressure mass spectrometer have yielded information regarding the kinetics of associative ionization reactions involving excited nitrogen molecules and helium atoms and of the formation of ion complexes by excited nitrogen molecular ions. The mobilities and formation of complex negative ions in  $O_2$  was also investigated (29).

#### E. Experimental and Analytical Techniques

A very important part of the work carried out under this contract has been the development and improvement of experimental and analytical techniques for the study of electron and ion collision processes. Among the new experimental techniques were a) the trapped-electron (2,4,6,10) and double electrostatic analyzer (16,19,21,22,24,26,27,30) apparatus for the study of inelastic collisions using nearly monoenergetic electrons, b) the cross field analyzer (23,34,38) for the measurement of the kinetic energies of fragment ions produced by dissociative attachment, c) the high temperature collision chamber (Section II) for the study of dissociative attachment of molecules with high rotational and vibrational temperatures, d) the low temperatures drift tubes (1,5,12,13,29) for the measurement of electron transport coefficients at the low electron energies characteristic of the ionosphere, e) the use (14) of electron attachment in  $SF_6$  as an indicator of the formation of low energy electrons and f) the application (15,30,31,34,36,Section II) of a high pressure mass spectrometer to the quantitative study of electron attachment and excitation and of the reactions of excited molecules and ions.

Among the new analytical procedures are techniques for the determination of elastic and inelastic collision cross sections from electron transport coefficients (5,9,17,20,25,35), and techniques for the prediction of electron and ion currents in a high pressure collision chamber (32).



## II. RECENT UNPUBLISHED RESULTS

### A. Temperature Dependence of Dissociative Attachment in $N_2O$

The effect of the gas temperature on the reaction  $e + N_2O \rightarrow O^- + NO$  has been studied in two separate experimental systems covering a total range from approximately 150°K to 1000°K. A brief description of each system follows.

#### The Wien Filter-Mass Spectrometer System

This system has been described in some detail previously (34, 38). With this system total collection measurements and mass analysis together with ion kinetic energy analysis may be performed. The gas enters the collision chamber through a copper tube of 1.2 cm outside diameter and 0.3 cm inside diameter and of total length 28 cm, of which 8 cm projects outside the vacuum wall of the system. The gas temperature is varied by either heating or cooling the external part of the copper tube, which is surrounded by a Dewar vessel. Two coolants were used in the present study, a mixture of solid  $CO_2$  and acetone, and liquid nitrogen. No direct indication of the temperature of the collision chamber was available. Indications are that the gas temperature in the collision chamber is somewhere between room temperature and the temperature of the copper tube. For example, previous work in which  $O_2$  was cooled with liquid nitrogen (77°K) by the same technique gave data consistent with the gas temperature in the collision chamber being 160°K. Data taken in  $N_2O$  using oil heated to 440°K in the Dewar vessel is consistent with data taken at 370°K in the second system, as described below. Despite the uncertainty in this first system as to the extent by which the gas temperature has been raised or lowered from that of the room the data show clearly that the shape of the cross section is temperature sensitive even at temperatures below 300°K.

### The High Temperature System

This system provides variation of the gas temperature from room temperature to approximately 2000°K by direct current heating of the collision chamber. This consists of an Iridium tube of wall thickness 0.0015". The temperature of the collision chamber is indicated by an Ir:Ir,Rh thermocouple attached to the wall of the tube. The electron beam traverses the collision chamber, entering and leaving via small holes in the wall. Ions are extracted by a small penetration field through a slit aligned with the electron beam. The ions are detected by a differentially pumped quadrupole mass spectrometer having a secondary electron multiplier at the output. The ion counts are fed to a multichannel analyzer with which automatic RPD data collection is performed. This technique is described below with reference to the work on ozone.

That the shape of the cross section observed with the mass spectrometer is not seriously affected by ion energy discrimination affects has been checked at room temperature by comparison of the observed shape with that obtained by the total collection measurements performed on the first system described above. Excellent agreement was obtained.

### Results

The shapes of the cross section observed at six different temperatures are shown in Fig. 1 by the six solid curves. Curves 1 through 4 were obtained by total collection measurements. Curves 5 and 6 were obtained mass spectrometrically on the high temperature system.

A serious difficulty which arises in such studies as these is that of accurately establishing the variation with temperature of the relative magnitude of the cross section, due to variation with temperature of the collision chamber pressure and, possibly, of ion collection efficiency. It was established with some confidence that the cross section at the 2.25 eV peak did not change with temperature in the range of temperatures accessible to the total collection

measurements. In constructing Fig. 1 from the measured shapes it has been assumed that this holds true at all temperatures studied. Even with this assumption the relative magnitude of the highest temperature curve shown could only be established approximately, by normalization to the trailing edge of the 2.25 eV peak, since clearly the peak is distorted by the temperature enhanced contribution. For this reason still higher temperatures have not yet been studied. A further difficulty of interpretation of higher temperature data, already evident in Curve 6 of the figure, is that the attachment peak at zero energy is so narrow that the measured height is clearly a function of the electron energy resolution.

The cross sections measured previously with total collection techniques by Schulz (6) and by Rapp and Briglia<sup>\*</sup> are also shown in the figure. Reasonable agreement exists between the present room temperature data and that of Rapp and Briglia. The data of Schulz, taken nominally at room temperature is consistent with data taken in the high temperature system at an indicated temperature of approximately 380°K.

It is clear from the above that considerable caution is indicated when applying dissociative attachment data taken at one temperature, usually nominally room temperature, to situations in which the gas is at some other temperature. The present work represents the second reaction<sup>\*\*</sup> for which it has been clearly established that the cross section is significantly enhanced at elevated gas temperatures.

#### B. Dissociative Attachment in Ozone

The reactions  $e + O_3 \rightarrow O^- + O_2$  and  $e + O_3 \rightarrow O_2^- + O$  have been studied using monoenergetic electron beam techniques with total collection and mass analysis of the product ions. The only previous electron beam study of these reactions was that by Curran (7) using the

<sup>\*</sup>D. Rapp and D. D. Briglia, J. Chem. Phys. 43, 1480 (1965).

<sup>\*\*</sup>W. L. Fite, R. T. Brackman and W. R. Henderson, Prov. IV International Conference on Physics of Electronic and Atomic Collisions. (Science Bookcrafters, Inc., New York, 1965), p. 100.

Retarding Potential Difference (RPD) technique to reduce the effective energy spread of the electron beam and a conventional mass spectrometer ion source. The energy resolution obtained in the present experiment (Full Width = 0.15 eV) using the RPD technique is significantly better than in the experiment of Curran (Full Width = 0.45 eV). This improvement arises mainly from the use in the present experiment of a more sophisticated collision chamber, in which the ion extraction field is supplied by a parallel plate configuration rather than by a single "pusher" electrode. A further advantage of this design is that "total collection" measurements may be made of the ion current to the appropriate parallel plate using the same extraction field condition as employed for mass analysis. Such "total" measurements together with the present facility for absolute measurement of the collision chamber pressure allow a determination of the cross section to be made.

The various aspects of the present work are summarized below.

#### The Automated R.P.D. Technique

The present experiment employs an automated procedure for obtaining R.P.D. data. The heart of the system is CAT 400 C multi-channel analyzer whose internally generated channel advance pulses sweep the analyzer alternately in the add and subtract modes. The difference electron current and the corresponding difference ion current are accumulated as functions of the electron energy by using digital to analog conversion of the "live" channel address to generate a staircase electron accelerating voltage waveform. An important advantage of this system is that the electron energy may be swept twice (add, subtract) in a time short compared to possible drifts in electron current, collision chamber pressure, multiplier sensitivity, etc., yet data may be accumulated over an arbitrarily long period, thereby improving the signal to noise ratio. This aspect was of value in the present experiment due to the difficulty of maintaining the ozone pressure in the collision chamber constant over long periods. Determinations of the shape of the cross section for attachment and

of the relative contributions of  $O^-$  and  $O_2^-$  production to the total could be made without regard to the relative partial pressures of  $O_3$  and its decomposition product  $O_2$ , since  $O_2$  does not dissociatively attach in the electron energy range of primary interest here, i.e., between 0 and 4 eV.

#### Relative Contributions of $O^-$ and $O_2^-$

Mass spectrometric determinations of the shape and relative magnitudes of dissociative ionization cross sections will in general suffer from two sources of error. Firstly, if the ions are formed with significant kinetic energy depending on the electron energy, energy discrimination by the mass spectrometer will distort the shape of the observed cross section. Secondly, the detection sensitivity of the mass spectrometer is likely to be mass dependent, especially if a secondary electron multiplier is employed at the output. A study of the kinetic energy distributions of  $O^-$  and  $O_2^-$  from  $O_3$  revealed that  $O_2^-$  is formed with near thermal energies, the distribution being rather insensitive to the electron energy. A similar result was obtained for  $O^-$  except that at electron energies in excess of 2 eV a second peak in the ion energy distribution was observed.\* It was concluded from these observations that the mass spectrometer observations should give the shape of the cross section rather accurately for  $O_2^-$  at all relevant electron energies, and similarly for  $O^-$  at the lower electron energies.

The relative contribution of  $O^-$  to the total cross section was determined by using mixtures of  $O_3$  and  $CO_2$ . It is known from previous work that  $O^-$  is produced from  $CO_2$  in the region of 4-5 eV with a near thermal kinetic energy distribution. It could, therefore, be assumed that  $O^-$  ions from  $O_3$  and  $CO_2$  are detected by the mass

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\*The position of this second peak was dependent on the electron energy in a manner consistent with it arising from a separate dissociative attachment process in which most and possibly all the excess energy of reaction appears as kinetic energy of separation of the fragments. A search was made unsuccessfully for a similar peak in the  $O_2^-$  distribution.

spectrometer with equal efficiencies, in which case the total ion current and  $O^-$  mass spectrometer signals arising from  $CO_2$  may be used to calibrate the  $O^-$  current from  $O_3$  in terms of equivalent total ion current. In this way it was determined that the ratio of the total attachment cross section at its peak to that of the contributing  $O^-$  production cross section at its peak is 1.6.

The relative magnitudes of the total and partial attachment cross sections are shown in Fig. 2. The shapes of the three full curves shown are given directly by the measurements. The curve labelled  $Q_a$  is the total attachment cross section whose shape is given by the total ion current measurements. The curves labelled  $O^-/O_3$  and  $O_2^-/O_3$  are from the mass spectrometer. The ratio of the peaks of  $Q_a$  to  $Q(O^-/O_3)$  is that prescribed by the above determination. The  $O_2^-$  peak has been scaled to obtain agreement at the lower energies between the measured  $Q_a$  and the sum of  $Q(O^-/O_3)$  and  $Q(O_2^-/O_3)$ , given by the broken curve. Below 1.3 eV the broken curve and the full curve  $Q_a$  are indistinguishable.

The discrepancy at higher energies is due, at least in part, to the high kinetic energy  $O^-$  production process mentioned earlier, and could plausibly be added to the  $Q(O^-/O_3)$  curve. It is gratifying to note that the relative contribution of  $O^-$  to  $Q_a$  determined by the above means accounts very closely for the total ion current observed below the threshold for  $O_2^-$  production.

The ratios, at their peaks of  $Q_a : Q(O^-/O_3) : Q(O_2^-/O_3)$  are 1.6:1:0.75. The ratio given by Curran for  $Q(O^-/O_3) : Q(O_2^-/O_3)$  is 0.64, in reasonable agreement with the above.

#### Calibration of the Cross Sections

In order to determine the absolute values of the cross sections from the present experiment, it was necessary to calibrate the total ion current measurements using a known cross section. For this purpose the 4.4 eV  $O^-$  peak in  $CO_2$  was chosen. It is known (8,\*) to

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\* D. Rapp and D. D. Briglia, J. Chem. Phys. 43, 1480 (1965).

have a peak value of  $1.5 \times 10^{-19} \text{ cm}^2$ , and by virtue of the similar ion energies involved the total ion collection efficiency may be expected to be the same as in  $\text{O}_3$ .

The most difficult part of the cross section determination was that involving the determination of the partial pressures of  $\text{O}_3$  present in the collision chamber. The total pressure of  $\text{O}_3$  plus its decomposition product,  $\text{O}_2$ , was measured directly by the Baratron. A number of techniques for estimating the partial pressure of  $\text{O}_2$  were tried. Of these, the most successful consisted of monitoring the  $\text{O}_2^+$  production rate with the mass spectrometer at an electron energy between the onsets for  $\text{O}_2^+$  from  $\text{O}_2$  and  $\text{O}_3$ .

The attachment cross section in  $\text{O}_3$  was determined by the above technique to have a peak value of  $(2.8 \pm 0.7) \times 10^{-17} \text{ cm}^2$ . The limits of error arise mainly from the difficulty of determining the ozone partial pressure. It should be borne in mind that the above value has been obtained relative to previous determinations of the cross section in  $\text{CO}_2$ , and will contain any error involved therein.

According to the present data the attachment cross section is finite very close to zero electron energy, with a value at 0.1 eV of about  $2.5 \times 10^{-18} \text{ cm}^2$ , corresponding approximately to a rate coefficient of  $5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ . The electron swarm experiment of Moruzzi and Phelps\* gave a value which is seven times smaller. This discrepancy is too large to be accounted for by the approximate nature of the comparison. It is clear from the work on  $\text{N}_2\text{O}$  reported above that there is a possibility that the discrepancy arises from a dependence on gas temperature.

#### Production of $\text{O}^-$ from $\text{O}_3$ at Higher Electron Energies

A second dissociative attachment peak, apparently not observed by Curran, has been found at higher electron energies. It peaks at 7.2 eV and arises from the reaction  $e + \text{O}_3 \rightarrow \text{O}^- + (?)$ . The neutral fragment could be either  $\text{O}_2$  or  $\text{O} + \text{O}$ . In the present experiment it is easily distinguishable from the nearby  $e + \text{O}_2 \rightarrow \text{O}^- + \text{O}$

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\* J. L. Moruzzi and A. V. Phelps, Bull. Am. Phys. Soc. 13, 209 (1968).

reaction (peak at 6.7 eV) by virtue of the available ion kinetic energy analysis. The  $O^-$  ions produced from  $O_3$  in this energy range have a kinetic energy distribution which peaks close to zero energy, making it easily resolvable from the  $O^-$  distributions produced from  $O_2$ . At its peak this reaction has a cross section smaller than the total attachment cross section at 1.1 eV by a factor of 12, corresponding to a value of approximately  $2.3 \times 10^{-18} \text{ cm}^2$ .

### C. High Pressure Beam Experiment

The objective of this experiment is to develop and use a new technique for making quantitative measurements of total inelastic collision cross sections. At present there are no techniques available for the measurement of total excitation cross sections over a wide range of electron energies. For example, the Maier-Leibnitz technique is limited to electron energies below that at which positive ions are formed. The method to be used is based upon determinations of the pressure dependence of the density of those electrons retaining the energy with which they are injected into a high pressure collision chamber. The depletion of this density below the level expected to result from elastic collisions alone provides a measure of the inelastic collision cross section. The density of initial energy electrons is monitored by measuring the current of ions produced in a known volume of the collision chamber.

Exploratory measurements of this type in a simple high pressure mass spectrometer ion source (36) indicated that the technique is capable of quantitative cross section determinations but that the apparatus used was not the optimum design. To this end a completely new system has been designed and built during the past year. It resembles a differentially pumped Tate and Smith apparatus, in that the current of ions reaching an extended collector plate is measured. In addition, the ion currents produced in three separate restricted volumes, spaced equally along the electron beam direction are monitored by measuring the ion currents arriving at three collector cups situated behind appropriately spaced slits in the planar collector



system. This arrangement permits spatial resolution studies of the ion production rate and allows a check that the electron transport in the collision chamber is occurring in a manner consistent with theory (32).

Tests of the original design of the tube indicated the presence of two problems. Firstly, the large mesh-covered hole in the exit plate of the collision chamber intercepted and could reflect a significant fraction of the elastically scattered electrons, thereby complicating the theoretical analysis of the pressure dependence of the ion currents and the transmitted electron current. Secondly, in the spatially resolved ionization studies at high pressure it was found that a significant fraction of the ions collected from the region adjacent to the exit plate were due to a back-flow of ions from the electron collector region. Attempts to correct this by the imposition of a suitable potential barrier were unsatisfactory in that efficient collection of the electrons could not be maintained. In order to correct these faults the electron collector and collision chamber exit plate were rebuilt. The electron path between the exit plate and the electron collector has been greatly reduced so as to minimize the extraneous ionization occurring in this region. The new exit plate has a hole of reduced size, across which are strung 0.001" diameter wires spaced 0.04" apart and aligned with the entrance slit. With this arrangement essentially complete transmission of both unscattered and scattered electrons is achieved under most conditions.

Work on this system is continuing under the current contract which started in September 1968.

#### D. Future Work

During the year September 1, 1968 through August 31, 1968, under Contract Number N00014-68-C-0490, studies will be made of the total inelastic collision cross section in oxygen, nitrogen, and subject to feasibility, in vapors such as  $\text{SF}_6$  and teflon. Studies will also be carried out of the temperature dependence of electron attachment in various gases including  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{SF}_6$ .

The work on inelastic collisions will be done using the high pressure electron beam experiment on which work was commenced during the final year covered by this report. An account of progress to data is included in Section II C. The temperature dependence studies will be made using the two systems employed in the study of  $N_2O$  described in Section II A.

### III. ABSTRACTS OF PUBLISHED PAPERS

The abstracts of papers published under Contract Nonr-2584(00) between June 1, 1958 and August 30, 1968 are given below. The abstracts are numbered with the number of the associated technical report.

1. "Measurement of the Attachment of Slow Electrons in Oxygen", Phys. Rev. Letters 2, 234 (1959) by L. M. Chanin, A. V. Phelps and M. A. Biondi.

Electron attachment coefficients in oxygen have been measured using a drift tube technique. At average electron energies below about 1 eV the attachment occurs by a three-body process. At energies above 1 eV the attachment process is a two-body process, presumably, dissociative attachment as found by electron beam techniques.

2. "Measurement of Excitation of N<sub>2</sub>, CO, and He by Electron Impact", Phys. Rev. 116, 1141 (1959) by G. J. Schulz.

The inelastic excitation of N<sub>2</sub> and CO by electron impact is studied using the trapped-electron method. In this method those electrons which have lost a portion of their initial energy in an inelastic collision are trapped in a potential well. Well depths up to 3 volts are used in the present experiment. The operation of the apparatus is checked for helium, where the shape of the excitation function is known accurately. The shape of the excitation function for metastable helium atoms obtained by the trapped-electron method is in good agreement with previous results. A large inelastic peak is observed at 2.3 eV in N<sub>2</sub> and 1.7 eV in CO. This phenomenon is discussed in terms of the formation of a temporary negative ion state of N<sub>2</sub> or CO and subsequent decay into various vibrational levels of the molecule. This model explains the sharp peak in both the elastic and inelastic cross section in N<sub>2</sub> and CO. Neither O<sub>2</sub> nor H<sub>2</sub> show such a sharp peak at low energies.

3. "Calculation of Propagation Constants for Electromagnetic Waves in Weakly Ionized Air", J. Appl. Phys. 31, 1723 (1960) by A. V. Phelps.

Formulas and graphs are given for the calculation of the propagation constants of an electromagnetic wave in weakly ionized, dry air at ionospheric temperatures in the presence of a magnetic field. Experimental studies of electron collision frequencies in nitrogen and oxygen are reviewed and used to obtain the magnitude and energy dependence of the electron collision frequency in air. The equations for the components of the conductivity tensor are developed taking into account the approximately linear dependence of the electron collision frequency on electron energy. Expressions derived on this assumption are found to be accurate except at low temperatures, high pressures, and low frequencies. The errors resulting from the use of an effective value for the energy independent collision frequency in the Appleton-Hartree equations are evaluated. Procedures are given for the calculation of the propagation constants for electromagnetic waves propagated parallel to and perpendicular to the magnetic field. These results are then applied to the derivation of relations required to reanalyze the ionospheric collision frequency measurements reported by Kane. The use of an effective collision frequency is found to lead to errors comparable to the experimental errors in the ionospheric observations.

4. "Excitation and Negative Ions In  $H_2O$ ", J. Chem. Phys. 33, 1661 (1960) by G. J. Schulz.

By combining the trapped-electron method with the study of negative ions and positive ions, it is possible to obtain data which can be used for construction of an approximate potential energy diagram of molecules. The experimental methods used are described and the  $H_2O$  molecule is discussed. The negative ion current peaks at  $6.5 \pm 0.1$  and  $8.8 \pm 0.1$  ev. Kinetic energy measurements on the negative ions show that the latter peak is associated with the same state at infinite separation as the first peak. The inelastic loss processes are essentially in agreement with optical absorption experiments. An inelastic process with a threshold at about 3.4 ev is observed.

5. "Drift Velocities of Slow Electrons in Helium, Neon, Argon, Hydrogen, and Nitrogen", Phys. Rev. 121, 798 (1961) by J. L. Pack and A. V. Phelps.

The drift velocities of electrons in helium, neon, argon, hydrogen, and nitrogen have been measured for  $E/p$  values between  $10^{-4}$  and 10 volt/cm-mm Hg at temperatures between 77°K and 373°K. The data were obtained from measurements of electron transit time in an improved version of the double-shutter tube developed by Bradbury and Nielsen. By applying sufficiently small voltage pulses to the control grids, it was possible to eliminate end effects present in previous experiments. Values of the momentum transfer cross sections for electrons with energies between about 0.003 and 0.05 ev are obtained which are consistent with the measured drift velocities for thermal electrons in helium, argon, hydrogen, and nitrogen. The derived momentum transfer cross section for electrons in helium is found to be independent of electron energy and equal to  $5.3 \times 10^{-16} \text{ cm}^2$ . The momentum transfer cross sections for argon, hydrogen, and nitrogen vary with electron energy.

6. "A Study of the  $\text{N}_2\text{O}$  Molecule Using Electron Beams", J. Chem. Phys. 34, 1778 (1961) by G. J. Schulz.

Inelastic processes and negative ion formation in  $\text{N}_2\text{O}$  are measured using the trapped-electron method and conventional techniques, respectively. A large inelastic process is observed at 2.2 ev and is interpreted as the formation of vibrationally excited  $\text{N}_2\text{O}$  via the formation of a temporary negative ion state. Negative ions  $\text{O}^-$  are observed beginning at zero ev with peaks of the negative ion current occurring at 0.7 and 2.2 ev. The latter peak is attributed to the formation of the temporary negative ion with subsequent decay into a stable  $\text{O}^-$  plus  $\text{N}_2$  in various states of vibrational excitation. Measurements of the kinetic energy of the negative ions confirm this hypothesis. A value of the dissociation energy of the  $\text{N}_2\text{-O}$  bond in  $\text{N}_2\text{O}$  is found from the appearance potential of  $\text{O}^-$  extrapolated to zero kinetic energy. This value,  $D(\text{N}_2\text{-O}) = 1.2 \pm 0.2 \text{ ev}$ , agrees within experimental error with the value of  $1.3 \pm 0.2$  found independently by Curran and Fox, but disagrees with the thermochemical value of 1.66 ev.

7. "Negative Ion Formation in Ozone", J. Chem. Phys. 35, 1849 (1961) by R. K. Curran.

Negative ion formation in ozone was studied in a mass spectrometer. Negative ions of O, O<sub>2</sub><sup>-</sup>, and O<sub>3</sub><sup>-</sup> were observed. The appearance potentials of O<sup>-</sup> and O<sub>2</sub><sup>-</sup> are 0 ev and 0.42±0.03 ev, respectively. The data on O<sup>-</sup> formation yield D(O<sub>2</sub>-O) ≤ 1.02±0.15 ev and the data on O<sub>2</sub><sup>-</sup> formation lead to a limiting value for the electron affinity of O<sub>2</sub> of EA(O<sub>2</sub>) ≥ 0.58 ev.

8. "Cross Sections and Electron Affinity for O<sup>-</sup> Ions from O<sub>2</sub>, CO, and CO<sub>2</sub> by Electron Impact", Phys. Rev. 128, 178 (1962) by G. J. Schulz.

Cross sections for the formation of O<sup>-</sup> from O<sub>2</sub>, CO, and CO<sub>2</sub> have been measured using an electron beam experiment in which an attempt is made to eliminate kinetic energy and angular discrimination by collecting most of the positive and negative ions produced in the tube. The cross sections are independent of electron current, pressure, and magnetic field. The values of these cross sections at their peak are 1.3 x 10<sup>-18</sup> cm<sup>2</sup> at 6.7 ev in O<sub>2</sub>, 1.6 x 10<sup>-19</sup> cm<sup>2</sup> at 10.1 ev in CO, and 4.5 x 10<sup>-19</sup> cm<sup>2</sup> at 8.2 ev in CO<sub>2</sub>. O<sup>-</sup> from CO<sub>2</sub> exhibits a second smaller peak at 4.2 ev with a cross section of 1.5 x 10<sup>-19</sup> cm<sup>2</sup>. Kinetic energy measurements on the O<sup>-</sup> ion from O<sub>2</sub> and CO<sub>2</sub> are not compatible with the value for the electron affinity (1.465 ev) obtained from photodetachment experiments but yield an electron affinity of 2.0±0.1 ev and so suggest the existence of excited states of O<sup>-</sup>. The experimental evidence from triatomic molecules N<sub>2</sub>O, NO<sub>2</sub>, and SO<sub>2</sub> is reviewed and is consistent with the higher value for the electron affinity for oxygen.

9. "Rotational Excitation and Momentum Transfer Cross Sections for Electrons in H<sub>2</sub> and N<sub>2</sub> from Transport Coefficients", Phys. Rev. 127, 1621 (1962) by L. S. Frost and A. V. Phelps.

Rotational excitation and momentum transfer cross sections for low-energy electrons in hydrogen and nitrogen are obtained from a comparison of theoretical and experimental values for the mobility and the diffusion coefficients. The theoretical values of the transport coefficients were obtained by calculating accurate electron energy

distribution functions using an assumed set of elastic and inelastic cross sections. The discrete nature of the energy loss occurring in a rotational or vibrational excitation collision was included in the theory, as were collisions of the second kind with thermally excited molecules. The resulting values of drift velocity and characteristic energy,  $D/\mu$ , were compared with experimental data and adjustments made in the assumed cross sections until good agreement was obtained. The momentum transfer cross sections found in this manner agree well with several recent analyses valid in restricted energy ranges. The final values of the rotational excitation cross sections are 2.5 times the values computed using the theory of Gerjuoy and Stein and the latest available values for the molecular electric quadrupole moments. In hydrogen, the analysis has been extended to energies for which vibrational excitation is important. A vibrational cross section with a maximum of roughly  $5 \times 10^{-17} \text{ cm}^2$  at 3 eV is consistent with the measurements.

10. "Excitation of Vibrational and Electronic Levels in  $\text{O}_2$  by Electron Impact", Phys. Rev. 128, 174 (1962) by G. J. Schulz and J. T. Dowell.

Low energy inelastic collisions between electrons and oxygen molecules are studied using the trapped-electron method. Peaks in the trapped-electron current are interpreted as vibrational excitation of the oxygen molecule to the states  $v = 1$  to  $v = 8$ . Two of these peaks can be attributed in part to the excitation of the  $^1\Delta_g$  and  $^1\varepsilon_g^+$  states. Approximate cross sections at 0.16 eV above threshold are less than  $3 \times 10^{-20}$  and  $6 \times 10^{-21} \text{ cm}^2$  for the  $^1\Delta_g$  and  $^1\varepsilon_g^+$  states, respectively. For electronic states above 5 eV, the cross sections at 0.16 eV above threshold are of the order of  $10^{-18} \text{ cm}^2$ .

11. "Drift Velocities of Slow Electrons in Krypton, Xenon, Deuterium, Carbon Monoxide, Carbon Dioxide, Water Vapor, Nitrous Oxide, and Ammonia", Phys. Rev. 127, 2084 (1962) by J. L. Pack, R. E. Voshall and A. V. Phelps.

The drift velocities of electrons in krypton, xenon, deuterium, carbon monoxide, carbon dioxide, water vapor, nitrous oxide, and ammonia

have been measured for  $E/p$  values between  $2.5 \times 10^{-4}$  and 30 volts/cm-mm Hg at temperatures between 77°K and 443°K. The data were obtained from measurements of electron transit times in a double-shutter drift tube. Values of the momentum transfer cross section as a function of electron energy for electrons with energies between about 0.003 and 0.08 eV are obtained which are consistent with the measured drift velocities for thermal electrons in all the gases reported.

12. "Ratio of the Diffusion Coefficient to the Mobility Coefficient for Electrons in He, A,  $N_2$ ,  $H_2$ ,  $D_2$ , CO, and  $CO_2$  at Low Temperatures and Low  $E/p$ ", Phys. Rev. 128, 2661 (1962) by R. W. Warren and J. H. Parker, Jr.

$D/\mu$ , the ratio of the diffusion coefficient to the mobility coefficient for electrons, has been determined as a function of  $E/p$ , the ratio of the electric field to pressure, in He, A,  $N_2$ ,  $H_2$ ,  $D_2$ , CO, and  $CO_2$ . Special interest is centered on the low temperature, low  $E/p$  data which are essential for the determination of low energy elastic and inelastic cross sections. The lowest temperature of operation is either 77°K or the boiling point of the gas being measured, whichever is higher. The lowest  $E/p$  value is well within the thermal range where  $D/\mu = kT/e$ . A careful analysis of the operation of the experimental tube is presented along with a method for removing inconsistencies in the results which arise from a conventional interpretation of the data.

13. Technical Report 13 entitled "Tables of Drift Velocities of Slow Electrons in Helium, Neon, Argon, Krypton, Xenon, Hydrogen, Deuterium, Nitrogen, Carbon Monoxide, Carbon Dioxide, Water Vapor, Nitrous Oxide, and Ammonia" by J. L. Pack, R. E. Voshall and A. V. Phelps was not intended for publication.

This report presents in tabulated form the drift velocities of electrons in various gases. The drift velocities were measured in helium, neon, argon, krypton, xenon, hydrogen, deuterium, nitrogen, carbon monoxide, carbon dioxide, water vapor, nitrous oxide, and ammonia for  $E/p$  values from  $10^{-4}$  to 30 volts/cm-mm Hg at several gas temperatures between 77°K and 443°K. In all gases except neon measurements were extended to low enough  $E/p$  such that the electrons were in thermal equilibrium with the gas.



14. "Formation of  $\text{SF}_6^-$  by Inelastically Scattered Electrons", J. Chem. Phys. 38, 780 (1963) by R. K. Curran.

Electrons which have undergone inelastic collisions with gas atoms and molecules are detected by adding small amounts of  $\text{SF}_6$  to the gas under study and by observing the energy dependence of the formation of  $\text{SF}_6^-$  ions. These experiments were carried out in a mass spectrometer designed to operate at pressures up to 1 Torr in the same region.

15. "Mass Spectrometer Investigation of Electron Impact Processes at Pressures to 1 mm Hg", J. Chem. Phys. 38, 2974 (1963) by R. K. Curran.

A mass spectrometer for the study of secondary reactions involving ions, excited species and molecules is described. The instrument was checked with the Hornbeck-Molnar process for  $\text{He}_2^+$  formation in He,  $\text{O}_3^+$  and  $\text{O}_4^+$  formation in  $\text{O}_2$  and  $\text{N}_3^+$  and  $\text{N}_4^+$  formation in  $\text{N}_2$ . Source pressures to about 1 mm Hg are used. The electron beam is controlled by the retarding potential difference technique for reducing the effective width in energy of the electron distribution.

16. "Resonance in the Elastic Scattering of Electrons in Helium", Phys. Rev. Letters 10, 104 (1963) by G. J. Schulz.

A sharp resonance in the cross section for the elastic scattering of electrons by helium is found using nearly monoenergetic electron beams. Observations at scattering angle of  $72^\circ$  show the resonance to occur at  $19.3 \pm 0.1$  ev.

17. "Elastic and Inelastic Collision Cross Sections in Hydrogen and Deuterium from Transport Coefficients", Phys. Rev. 131, 2115 (1963) by A. G. Engelhardt and A. V. Phelps.

By means of a numerical solution of the Boltzmann equation, elastic and inelastic collision cross sections have been derived for electrons in  $\text{H}_2$  and  $\text{D}_2$  subjected to a dc electric field. The cross sections for momentum transfer, rotational excitation, vibrational excitation, electronic excitation, and ionization are investigated by comparing experimental and theoretical values of transportation coefficients. The same momentum transfer cross section previously

obtained for  $H_2$  by Frost and Phelps has been found to be valid for  $D_2$ . Good agreement is secured between experiment and theory by multiplying the theoretical rotational cross sections of Gerjuoy and Stein by approximately 1.5 provided the polarization factor of Dalgarno and Moffet is used. The final cross section for vibrational excitation of  $H_2$  has a threshold at 0.52 eV and a peak of  $7.7 \times 10^{-17} \text{ cm}^2$  at 4.5 eV, whereas that of  $D_2$  has a threshold at 0.36 eV and a peak of  $6.6 \times 10^{-17} \text{ cm}^2$  at 4.7 eV. The derived electronic excitation cross sections are the same for both  $H_2$  and  $D_2$ . The ionization cross section was taken from the experimental results of Tate and Smith. Calculated transport coefficients for electrons subjected to crossed electric and magnetic fields, and high frequency ac electric fields are in agreement with recent experimental and theoretical results.

18. "Spatially Dependent Energy Distributions for Electrons Drifting Through a Gas in a Uniform Electric Field", Phys. Rev. 132, 2096 (1963) by J. H. Parker, Jr.

The steady state distribution function is obtained for electrons initially emitted from a point source into a neutral gas and which subsequently drift under the influence of a uniform dc electric field while undergoing elastic collisions with the gas atoms. The usual approximations are retained of regarding the distribution function as almost spherical in velocity space and of regarding the fractional energy gain or loss by an electron upon collision as small. However, the terms in the Boltzmann transport equation involving spatial derivatives of the distribution, which are usually assumed small in comparison to the field and collision terms, are treated exactly. The distribution function is given as a sum of energy modes, each of which decay with distance from the source. The lowest of these modes is the far-distant distribution, while the higher ones, which decrease more rapidly with distance, describe the decay of the initial source energy distribution. The complete distribution is obtained in terms of known functions in the case of an energy independent collision frequency, whereas in the energy independent cross section case, only the lowest mode is obtained. The far-distant part

of the distribution function is compared with the usual approximate expression which is obtained when the gradient terms are considered small and which is expressed as the density times a normalized energy function. It is shown, that when the gradient terms are correctly considered, the far-distant distribution in energy becomes position dependent. Furthermore, the deviation from the approximate theory becomes larger, the further the electrons are off the geometrical axis. This position dependence is most important when the electron energy is large in comparison to thermal energies. The interpretation of Townsend method for the determination of the ratio of the diffusion coefficient to the mobility,  $D/\mu$ , is re-examined on the basis of this more exact theory. It is shown that the error in  $D/\mu$  that results from using the conventional interpretation of this method under typical experimental conditions is never more than about 20%.

19. "Recent Studies of Vibrational Excitation of  $N_2$  by Electron Impact", Proceedings Sixth International Conference on Ionization Phenomena in Gases, Paris, July 1963 by G. J. Schulz.

The vibrational excitation of  $N_2$  by nearly monoenergetic electron beams has been studied at a scattering angle of  $72^\circ$ . These experiments provide the first data on the effect of the resonances near 2.3 eV on the cross sections for elastic scattering and for excitation of the lowest vibrational state.

20. "Transport Coefficients and Cross Sections in Argon and Hydrogen-Argon Mixtures", Phys. Rev. 133, A375 (1964) by A. G. Engelhardt and A. V. Phelps.

Using a method described previously the distribution function of electron energies for electrons in argon and mixtures of hydrogen and argon has been obtained by a numerical solution of the Boltzmann equation which takes into account elastic and inelastic collisions. By taking appropriate averages over the distribution function, the electron drift velocity  $w$ , magnetic drift velocity  $w_M$ , and characteristic energy  $\epsilon_K$  are computed. A comparison of calculated and experimental values of these transport coefficients enables us, in the case of pure argon, to extend the previous work of Frost and Phelps and derive the

momentum transfer cross section from 0.7 to 25.0 ev. The momentum transfer and inelastic collision cross sections derived in this paper for argon and previously for hydrogen give rise to transport coefficients in mixtures of these two gases which are consistent with most of the available experimental data.

21. "Resonances in the Elastic Scattering of Electrons on Atoms and Molecules", Atomic Collision Processes, edited by M.R.C. McDowell (North Holland Publishing Co., Amsterdam, 1964), p. 124 by G. J. Schulz.

This paper presents experimental evidence for the existence of compound states in simple atomic and molecular systems. The experimental evidence for these compound states comes from the observation of the elastic and inelastic cross section by electron impact. Once formed, the compound state can decay into any state of the atoms which lies below it; namely, back to the ground state of the atom or molecule (elastic scattering), to an electronically excited state of the atom or molecule, to vibrational states of the molecule, or to a negative ion plus a neutral fragment. The compound states discussed in this paper occur below the first electronically excited state of the atom or molecule; they have been observed in helium and neon atoms, and in the molecules nitrogen, carbon monoxide, and nitrous oxide.

22. "Vibrational Excitation of  $N_2$ , CO, and  $H_2$  by Electron Impact", Phys. Rev. 135, A988 (1964) by G. J. Schulz.

The cross section for vibrational excitation of  $N_2$ , CO, and  $H_2$  by electron impact is measured using a double electrostatic analyzer. Electrons are examined after scattering from the molecules at an angle of 72 degrees. Both  $N_2$  and CO exhibit a small vibrational cross section to the first state below 1.7 ev and 1.0 ev, respectively, which is attributed to direct excitation by electron impact. Above these energies, many vibrational states are excited and the cross section becomes large; it is postulated that the excitation proceeds via a compound state of  $N_2$  and CO. The peak of the cross section occurs at 2.3 ev in  $N_2$  and 1.75 ev in CO. In hydrogen, the cross section to the first vibrational state predominates; the cross section to the second vibrational state of  $H_2$  is about 14% of the first state, at an energy of 3.4 ev.

23. "Interpretation of Experiments on Dissociative Attachment or Ionization of Molecules", Phys. Rev. Letters 12, 449 (1964) by P. J. Chantry and G. J. Schulz.

This letter points out an error in the method normally used to relate the measured kinetic energy of fragments to the total energy released in dissociative reactions. In particular, it is shown that the thermal motion of the target molecule introduces a large spread in the kinetic energies of the fragments. When this effect is taken into account it is possible to reconcile the electron affinities obtained for atomic oxygen using electron beam techniques with the values obtained from measurements of the photodetachment threshold.

24. "Experiments on Resonances in the Elastic Cross Section of Electrons on Rare Gas Atoms", Phys. Rev. 136, A650 (1964) by G. J. Schulz.

Resonances in the elastic scattering are studied in a scattering experiment at an angle of 72 degrees for He and Ne and in a transmission experiment for He, Ne, Kr and Xe. These resonances result from a compound state of the rare gas atom and occur about 0.5 ev below the first excited state. The magnitude of the resonances can be enhanced in a transmission experiment when only the unscattered electrons are observed. It is pointed out that the resonance in helium can be used for a determination of the apparent electron energy distribution and as a calibration point on the electron energy scale.

25. "Momentum Transfer Cross Sections for Slow Electrons in He, Ar, Kr and Xe from Transport Coefficients", Phys. Rev. 136, A1538 (1964) by L. S. Frost and A. V. Phelps.

Momentum transfer cross sections for electrons in He, Ar, Kr, and Xe are obtained from a comparison of theoretical and experimental values of the drift velocities and of the ratio of the diffusion coefficient to the mobility coefficient for electrons in these gases. The theoretical transport coefficients are obtained by calculating accurate electron energy distribution functions for energies below excitation using an assumed energy dependent momentum transfer

cross section. The resulting theoretical values are compared with the available experimental data and adjustments made in the assumed cross sections until good agreement is obtained. The final momentum cross section for helium is  $5.0 \pm 0.1 \times 10^{-16} \text{ cm}^2$  for an electron energy of  $5 \times 10^{-3} \text{ ev}$  and rises to  $6.6 \pm 0.3 \times 10^{-16} \text{ cm}^2$  for energies near 1 ev. The cross sections obtained for Ar, Kr, and Xe decrease from  $6 \times 10^{-16}$ ,  $2.6 \times 10^{-15}$  and  $10^{-14} \text{ cm}^2$ , respectively, at 0.01 eV to minimum values of  $1.5 \times 10^{-17} \text{ cm}^2$  at 0.3 ev for Ar,  $5 \times 10^{-17} \text{ cm}^2$  at 0.65 ev for Kr, and  $1.2 \times 10^{-16}$  at 0.6 ev for Xe. The agreement of the very low energy results with the effective range theory of electron scattering is good.

26. "Resonances in the Inelastic Cross Section of Helium", Phys. Rev. Letters 13, 476 (1964) by G. J. Schulz and J. W. Philbrick.

This paper presents experimental evidence for structure in the inelastic cross section in helium which is interpreted in terms of compound states above the lowest electronically excited state. A study of the inelastically scattered electrons at an angle of 72 degrees shows that structure in the  $2^3\text{S}$  cross section exists for electron energies around 21 ev and 22.4 ev.

27. "Experiment on the Resonance in the Elastic Scattering of Electrons by Atomic Hydrogen", Phys. Rev. Letters 13, 583 (1964) by G. J. Schulz.

A resonance in the elastic scattering cross section of electrons in atomic hydrogen has been found at an energy of  $9.7 \pm 0.15 \text{ ev}$ . The energy of this resonance is in good agreement with the predictions of theory.

28. "Measurement of Cesium Excitation Cross Section Near Threshold by a Swarm Technique", Phys. Rev. 140, A792 (1965) by J. F. Nolan and A. V. Phelps.

Electron drift velocities have been measured in cesium-argon mixtures for E/N values between  $3 \times 10^{-19}$  and  $5 \times 10^{-18} \text{ V-cm}^2$  and cesium to argon concentration ratios between  $10^{-8}$  and  $10^{-5}$ . The drift velocity was obtained from measurements of the electron transit time using an ac technique which is a modification of a technique developed originally

by Rutherford for ion drift velocity measurements. Numerical solutions of the Boltzmann transport equation were used to determine an excitation cross section which is consistent with the experimental drift velocity data. For a single excitation threshold at 1.386 ev, the best slope for a linear cross section is  $7.1 \times 10^{-15} \text{ cm}^2/\text{ev}$ . If excitation to the  $6 P_{1/2}$  and  $6 P_{3/2}$  states is considered separately, with thresholds at 1.386 ev and 1.454 ev respectively, the linear cross sections obtained have a slope of  $2.5 \times 10^{-15} \text{ cm}^2/\text{ev}$  for  $6 P_{1/2}$  excitation, and  $5.0 \times 10^{-15} \text{ cm}^2/\text{ev}$  for  $6 P_{3/2}$  excitation. The range of validity of these values is from threshold up to about 1.8 ev. Other shapes for the cross section are investigated. The experimental cross section is in reasonable agreement with extrapolations of theoretical cross sections.

29. "Mobility of Negative Ions in  $\text{O}_2$  at Low  $E/N$ ", J. Chem. Phys. 43, 1990 (1965) by R. E. Voshall, J. L. Pack and A. V. Phelps.

Measurement of negative ion mobilities in pure  $\text{O}_2$  were made as a function of gas pressure (2-700 Torr), gas temperature (77.4 to 373°K), and electric field. Values of  $E/N$ , electric field over gas density, ranged from  $6 \times 10^{-19}$  to  $6 \times 10^{-17} \text{ V-cm}^2$  so that the ions were in thermal equilibrium with the gas. The ion mobility times gas density  $\mu N$  is independent of density for 195°K and above. Values of  $\mu N$  for this ion,  $\text{O}_2^-$ , are  $5.7 \times 10^{19}$ ,  $6.5 \times 10^{19}$ ,  $6.8 \times 10^{19} \text{ volt}^{-1} \text{ sec}^{-1} \text{ cm}^{-1}$  for temperatures of 195, 300 and 373°K, respectively. The density dependence of the measured mobilities at 77.4 and 87.6°K is consistent with an equilibrium between the concentrations of  $\text{O}_2^-$  and  $\text{O}_4^-$  ions. The low density data yield values of  $\mu N$  for the  $\text{O}_2^-$  ion of  $4.7 \times 10^{19}$  and  $4.9 \times 10^{19} \text{ volt}^{-1} \text{ sec}^{-1} \text{ cm}^{-1}$  at 77.4 and 87.6°K. The  $\mu N$  value of  $\text{O}_4^-$  ions is  $2.6 \pm 0.5 \times 10^{19} \text{ volt}^{-1} \text{ sec}^{-1} \text{ cm}^{-1}$  at both temperatures. Correlation with models for the internal motion of  $\text{O}_4^-$  leads to an estimated dissociation energy of  $0.06 \pm 0.02 \text{ ev}$ .

30. "Energy Levels of the Compound State of  $\text{N}_2$  Near 2.3 ev", J. Chem. Phys. 44, 1297 (1966) by G. J. Schulz and H. C. Koons.

This letter reports high accuracy measurements of the spacing of the structure in the elastic and vibrational excitation cross sections of  $\text{N}_2$  for electron energies with energies near the 2.3 ev resonance.

31. "Formation of  $H^-$  by Electron Impact on  $H_2$  at Low Energy", Phys. Rev. Letters 15, 946 (1965) by G. J. Schulz and R. K. Asundi.

This letter reports the formation of the atomic hydrogen negative ion by electron impact on  $H_2$  very close to the theoretical threshold for the production of  $H^-$  and  $H$  with zero kinetic energy via the process  $e + H_2 \rightarrow H^- + H$ . We find  $H^-$  formation with a very sharp onset at an electron energy of  $3.73 \pm 0.07$  eV and a very steeply rising, albeit small, cross section which peaks very close to its onset. This observation leads to a better understanding of the potential-energy curves of the  $H_2^-$  system and has a bearing on the interpretation of vibrational excitation in  $H_2$ .

32. "Theory of Electron Collision Experiments at Intermediate and High Pressures", Phys. Rev. 152, 81 (1966) by P. J. Chantry, A. V. Phelps and G. J. Schulz.

By means of a two stream approximation an analytical solution is obtained to the equation of transfer governing the steady state concentration of mono-energetic electrons within a slab of gas bounded by two infinite planes, one of which emits a constant current density normal to its surface. The theory places no restriction on the gas pressure and includes the effects of inelastic collisions and partial reflection of scattered electrons at one or both boundaries. The results are applied to electron beam experiments at intermediate and high pressures where the mean free path of electrons is comparable to or less than the length of the collision chamber. Analytical expressions are obtained for the electron current transmitted through the gas and for the normalized ion currents to be expected in the case of total ion collection and in the case of sampling through a slit. The effect of elastic and inelastic collisions may be represented by an "equivalent length factor" which modifies the equations normally applicable under low pressure conditions. The results of the present theory are compared with previous theories with particular reference to their use in interpreting experiments of the Maier-Leibnitz type, designed to measure absolute values of inelastic collision cross sections.



33. "Isotope Effect in the Dissociative Attachment in  $H_2$  at Low Energy", Phys. Rev. 158, 25 (1967) by G. J. Schulz and R. K. Asundi.

The dissociative attachment cross section for formation of  $H^-$  and  $D^-$  from  $H_2$ , HD, and  $D_2$  has been measured in the threshold range from 3.75 to 5 eV using a mass spectrometer for ion identification. A pronounced isotope effect is observed. The cross section of  $H^-$  from  $H_2$  has a peak value of  $1.6 \times 10^{-21} \text{ cm}^2$ ,  $D^-$  from HD,  $1 \times 10^{-22} \text{ cm}^2$ , and  $D^-$  from  $D_2$ ,  $8 \times 10^{-24} \text{ cm}^2$ , all peaks occurring at 3.75 eV. Negative ion formation in this energy range proceeds via the compound state,  $^2\Sigma_u^+$ , whose lifetime against autodetachment is calculated from the above cross sections to be about  $1 \times 10^{-15} \text{ sec}$ . Because of this short lifetime and the relatively long time needed for the atoms to separate, the probability of survival of the negative ion and therefore the dissociative attachment cross section in  $H_2$  at 3.75 eV is small. For the heavier isotopes the separation time is even longer and therefore the dissociative attachment cross section is minute. The same compound state is also responsible for vibrational excitation of the hydrogen molecule.

34. "Kinetic Energy Distribution of Negative Ions Formed by Dissociative Attachment and the Measurement of the Electron Affinity of Oxygen", Phys. Rev. 156, 134 (1967) by P. J. Chantry and G. J. Schulz.

The kinetic energy distribution of ions produced by a dissociative ionization process is derived, taking into account the effect of thermal motion of the target molecule. In the case of dissociative attachment of monoenergetic electrons to a diatomic molecule the width at half maximum of the negative ion energy distribution is given by  $(11\beta kT E_0)^{1/2}$  where  $\beta$  is the ratio of the mass of the ion to that of the present molecule,  $T$  is the target gas temperature, and  $E_0$  is the most probable ion energy. Using a crossed field velocity filter  $O^-$  ion energy distributions arising from the attachment of essentially monoenergetic electrons to  $O_2$  are studied as a function of electron

energy at two gas temperatures. The measured widths of the distributions are consistent with the above relationship. Measurements of  $E_0$  as a function of the electron energy allow a determination of the electron affinity,  $A$ , of atomic oxygen. The result,  $A = 1.5 \pm 0.1$  ev, is in excellent agreement with photodetachment threshold determinations.

35. "Momentum Transfer and Inelastic Collision Cross Sections for Electrons in  $O_2$ , CO, and  $CO_2$ ", Phys. Rev. 158, 70 (1967) by R. D. Hake, Jr. and A. V. Phelps.

Momentum transfer and inelastic collision cross sections for electrons in  $O_2$ , CO and  $CO_2$  are calculated from measured values of the electron drift velocity, characteristic energy, attachment coefficient, and ionization coefficient. The experimental data for  $O_2$  is most consistent with vibrational excitation cross sections consisting of a series of resonances located at the vibrational energy levels of the negative ion and having values of cross section times energy-half-width of the order of  $10^{-18} \text{ cm}^2\text{-ev}$ . The calculated effective dipole moment for rotational excitation of CO is in very good agreement with values obtained by other techniques. The vibrational excitation cross section for CO at electron energies below 1 ev is in agreement with theoretical predictions. The vibrational excitation cross sections required for consistency with the  $CO_2$  data are very large ( $2 - 5 \times 10^{-16} \text{ cm}^2$ ) and include a peak very close to the vibrational threshold of 0.083 ev.

36. "Studies of  $N_4^+$  and  $N_3^+$  Ion Formation in Nitrogen Using High Pressure Mass-Spectrometry", J. Chem. Phys. 47, 1584 (1967) by R. K. Asundi, G. J. Schulz and P. J. Chantry.

The formation of the complex ions of nitrogen  $N_4^+$  and  $N_3^+$  has been studied at pressures up to 0.1 torr using a differentially pumped mass spectrometer and monoenergetic electron-beam techniques. The  $N_4^+$  ion has an appearance potential of  $15.0 \pm 0.1$  ev, and exhibits a quadratic pressure dependence in the threshold region, consistent with the secondary reaction  $N_2^+ + N_2 \rightarrow N_4^+ + e$ . At electron energies greater than 17.5 ev, a cubic pressure dependence is observed, consistent with the secondary reaction  $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$ . The reverse of

this reaction has been shown to lead to an early onset of  $N_2^+$  when a sufficiently large extraction field is used to impart the necessary kinetic energy to the  $N_4^+$  ion. The  $N_3^+$  ion has an appearance potential of  $21.1 \pm 0.1$  eV and exhibits a quadratic dependence at low pressures, consistent with the secondary reaction  $N_2^+(^4\Sigma_u^+) + N_2 \rightarrow N_3^+ + N$ , proposed previously by Cermak and Herman. At higher pressures the  $N_3^+$  pressure dependence deviates from quadratic due to the depopulation of the  $N_2^+(^4\Sigma_u^+)$  state. An analysis of this deviation in the  $N_3^+$  pressure dependence provides an approximate estimate of the radiative lifetime of the  $N_2^+(^4\Sigma_u^+)$  of  $\tau = 8 \times 10^{-6}$  sec and of the collisional destruction rate coefficient  $(Q_D^v)_{AV} = 2 \times 10^{-9}$  cm<sup>3</sup>/sec.

37. "Rotational and Vibrational Excitation of Molecules by Low Energy Electrons", Rev. Mod. Phys. 40, 399 (1968) by A. V. Phelps.

Techniques for the determination of rotational and vibrational excitation cross sections of molecules by low-energy electrons are reviewed. The results of experiment are then compared with theory. High-energy resolution electron beam techniques are most useful for the measurement of the details of resonance-type, vibrational excitation cross sections. Cross section determinations from analyses of electron transport coefficients are most successful at energies near the threshold of vibrational excitation and for rotational excitation. High-frequency energy relaxation studies provide data on rotational excitation. A comparison of presently available experimental and theoretical results shows that some of the excitation processes, e.g., rotational excitation of  $N_2$  and CO and vibrational excitation of CO near threshold, are accurately described by the longest-range forces and Born approximation. In other cases, e.g., vibrational excitation of  $N_2$  and CO near 2 eV, the excitation is best described in terms of an electron resonance with the molecular potential.

38. "Dissociative Attachment in CO and NO", Phys. Rev. 172, 125 (1968) by P. J. Chantry.

The electron energy dependence of the cross sections and of the ion kinetic energy distributions have been measured for  $O^-$  production from CO and NO. The present apparatus permits total collection

measurements as well as kinetic energy analysis and mass identification of the ions produced. It is shown that in CO two reactions contribute to the single peak in the cross section, whereby carbon atoms are produced in their ground state and in their first excited state ( $^1D$ ) respectively. The first reaction is predominant, and known from previous work to have a peak cross section of  $2.0 \times 10^{-19} \text{ cm}^2$ . Normalized to this, the second reaction is shown to have a peak cross section of  $9.5 \times 10^{-21} \text{ cm}^2$ . In NO it is shown that  $O^-$  production proceeds exclusively through the reaction  $e + NO \rightarrow O^- + N^*$  where  $N^*$  is the first excited state ( $^2D$ ). No  $O^-$  ions are observed corresponding to the formation of ground state N. Nor is there any evidence for the production of the second excited state of nitrogen,  $N(^2P)$ , postulated by Dorman to account for the structure in the attachment cross section.

#### FIGURE CAPTIONS

- Fig. 1 - The dependence on temperature of the dissociative attachment cross section in  $N_2O$ . Curves 1 through 4 are the results of total ion collection measurements. Curves 5 and 6 were obtained from the high temperature source mass spectrometer.
- Fig. 2 - Relative total and partial attachment cross sections in ozone. The shapes of the three full curves are given directly by the measurements. The broken curve shows the sum of  $Q(O^-/O_3)$  and  $Q(O_2^-/O_3)$  where it differs from  $Q_a$ .

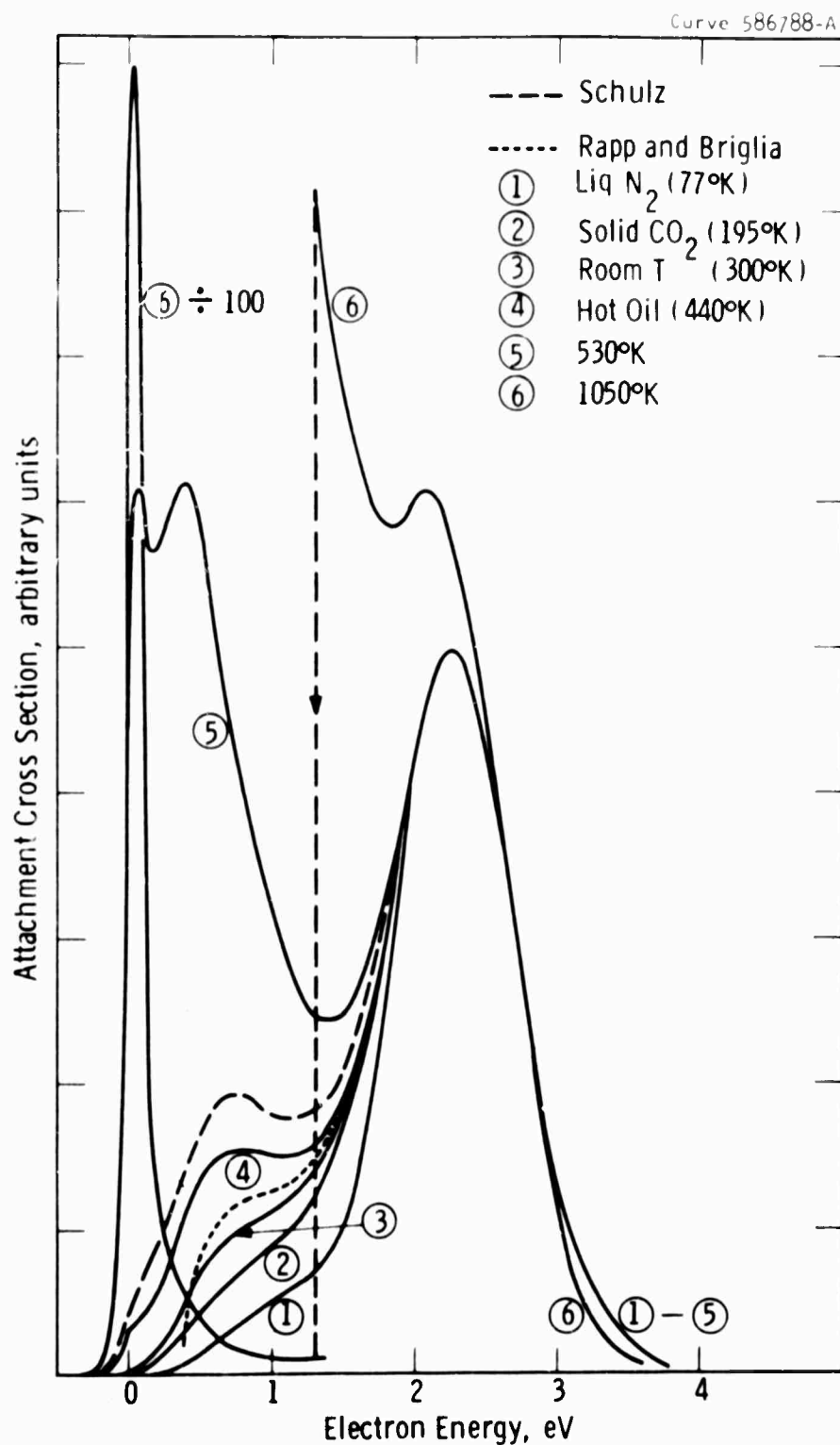


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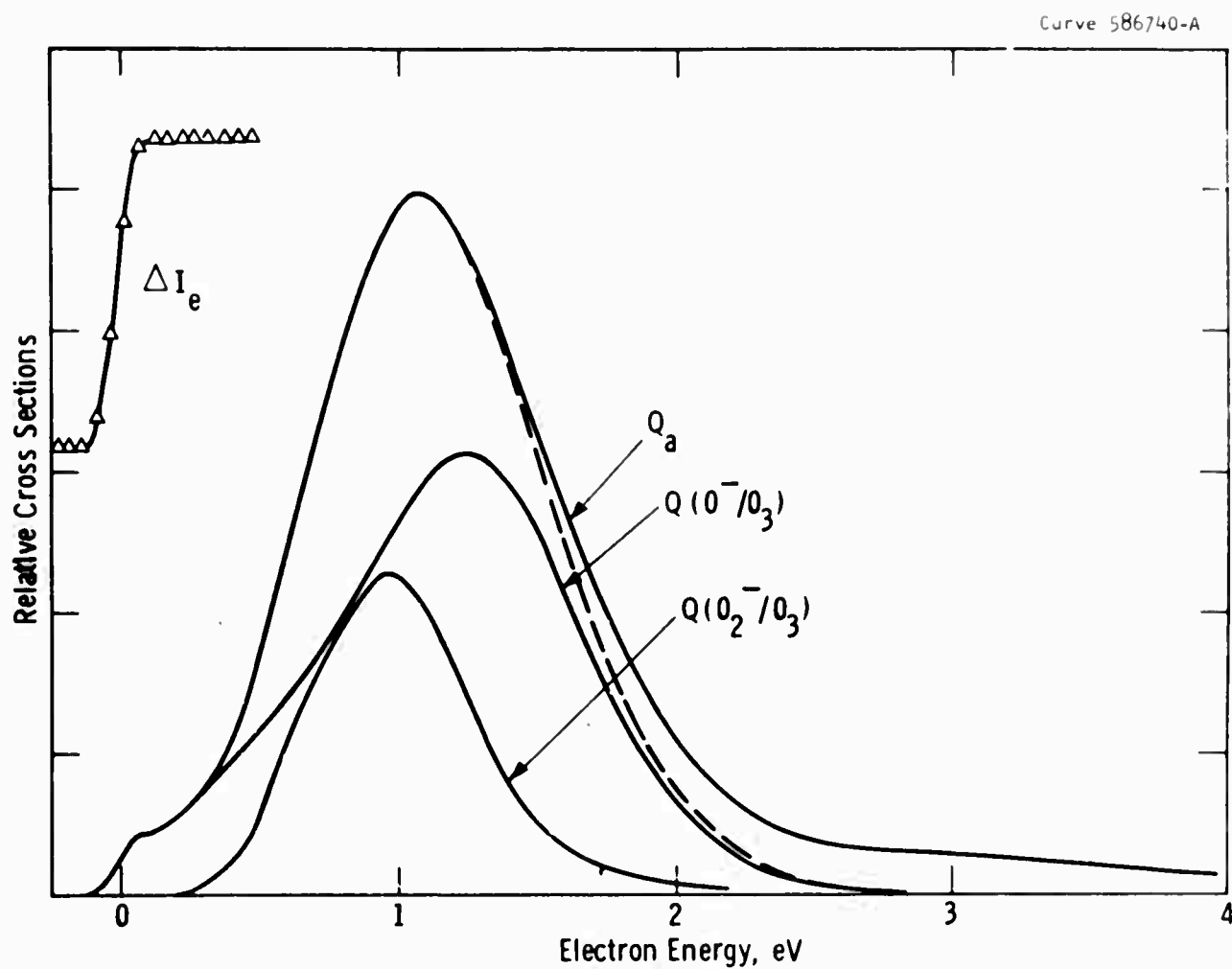


Fig. 2 - Relative total and partial attachment cross sections in ozone. The shapes of the three full curves are given directly by the measurements. The broken curve shows the sum of  $Q(O^-/O_3)$  and  $Q(O_2^-/O_3)$  where it differs from  $Q_a$ .

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13 ABSTRACT  This final report for Contract Nonr-2584(00) entitled Atomic Collision Processes Relating to the Ionosphere consists of a summary of the more important results obtained and a set of abstracts of the technical reports published under the contract. The published results include the experimental discovery of resonances in the elastic scattering cross sections of atoms and molecules, studies of the role of resonances in the determination of vibrational and electronic excitation cross sections and of cross sections for negative ion formation, and determinations of elastic and inelastic scattering cross sections for electrons in various gases such as N <sub>2</sub> , O <sub>2</sub> , CO <sub>2</sub> , and H <sub>2</sub> O. Recent unpublished results concerned with electron attachment in O <sub>3</sub> and N <sub>2</sub> O and with the development of a new technique for the measurement of inelastic scattering cross sections are discussed.			



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## KEY WORDS

Electrons  
Gases  
Atmospheric  
Cross Sections  
Attachment  
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